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(54) BIPOLAR ELECTRODE ASSEMBLIES IN GALVANIC BATTERIES

(71) We, ESB INCORPORATED, a corporation organised and existing under the law of the State of Delaware, United States of America, of 5 Penn Center Plaza, Philadelphia, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to galvanic batteries which include a plurality of bipolar electrode assemblies. In particular, it relates to multicell reserve batteries which operate by immersion in seawater.

There is a class of batteries employing zinc, aluminium or magnesium anodes and silver chloride, copper chloride or lead chloride cathodes which are activated by and operate submerged in a weak aqueous electrolyte such as seawater. Such batteries are completely inactive until immersion. Batteries of this type have been used in considerable quantity in ocean waters. The equipment with which they are associated is often of the non-recoverable sort. Also, the use period is often limited to a few hours.

It has been a prime objective of designers of such batteries to seek ways to simplify the construction of the batteries.

In a number of known devices, bipolar electrode assemblies are used. By this term is meant an assembly comprising the anode of a first cell, the cathode of a second cell and a barrier impervious to electrolyte located between the two electrodes. A number of such bipolar assemblies are piled together with terminal anode and cathode at opposite ends and the barriers properly sealed to a container resulting in a multicell battery. In many bipolar assemblies the barrier is a metal sheet contacting the anode on one side and the cathode on the other. This provides a very low resistance electrical path from anode to cathode of adjacent cells. It provides a strong support for both anode and cathode. However, the choice of metal is somewhat limited since it must be electrochemically compatible with both anode and cathode. It must be free from attack by the electrolyte, it must not passivate by contact with the electrolyte and it must avoid local action effects. Further, a metal barrier will add weight to the battery assembly when compared to a battery having non-metallic barriers. Bipolar plates having electrodes attached to either side of a moulded plastics barrier are known. With this design, a lip having a thickness equal to that of the length of a cell sub-assembly may be moulded about the periphery of the barrier. A battery is built from such bipolar subassemblies simply by cementing the lip of one barrier to that of the next. However, costly dies are required for the moulding of such barriers. Also, there is a limit to the thinness to which a moulded part can be made. The limit is about 0.5 mm or greater.

Batteries are known where a serious of bipolar electrode assemblies with barriers extending outwardly therefrom are dipped into a suitable plastic material for a short time. The plastic material bridges the gap from barrier to barrier and, upon setting, forms a shell or battery casing.

In accordance with the present invention, a galvanic battery comprises a housing and a plurality of bipolar electrode assemblies in the housing, each assembly comprising an anode and a cathode which are electrically connected to each other and are separated from each other by a barrier made of a sheet of flexible non-conductive material having two opposed side edges each of which is bent to form a flange, the assemblies being arranged parallel to each other, face to face with spaces between them, and with the flanges of each assembly other than an end assembly directed towards an adjacent assembly, the flanges together with adhesively coated tapes which are sealed to the flanges forming sidewalls of the housing.

The thickness of the barrier preferably lies within the range of 0.05 to 0.20 mm. and the material of the barrier is preferably polyethylene terephthalate.

The electrical connection between the

anode and the cathode preferably penetrates the barrier and holds the assembly together.

Endwalls with suitable electrodes attached thereto are preferably provided at both ends of the housing and the top and bottom of the housing are preferably sealed. Adhesive tape may be used to form the top wall and bottom wall of the housing or, alternatively, the battery may be dipped in a hot melt to close the top and bottom of the housing. The result is a simple, compact construction.

In order that the invention may be more clearly understood, some examples will now be described with reference to the accompanying drawings in which:

Figure 1 is a perspective view of a battery embodying the invention;

Figure 2 is a perspective view of a bipolar assembly of the battery;

Figure 3 is a cross section on line 3—3 of Figure 2;

Figure 4 is an elevation of an alternative bipolar assembly;

Figure 5 is a cross section on line 5—5 of Figure 1;

Figure 6 is a detail of Figure 5;

Figure 7 is a cross section on line 7—7 of Figure 1;

Figure 8 is a graph illustrating the discharge voltage of a lead chloride-magnesium battery embodying the invention; and

Figure 9 is a graph illustrating the discharge voltage of a silver chloride-magnesium battery embodying the invention.

Seawater batteries of the type described herein are single discharge devices. In Figure 1, a seawater battery 10 includes a sidewall 12a, a top 14 and an endwall 16. A second sidewall 12b, bottom 15 and second end wall 18 (see Figures 5 and 7) complete the external features of the battery. In the form illustrated in Figure 1, the endwalls are made of stiff plastics sheet and the sidewalls, the top and the bottom are one or more ribbons of adhesively coated insulating tape wrapped around the endwalls and thus containing the battery. In endwall 16, a top port 20 is shown near top 14 and sidewall 12a. A second port 22 is also shown near the bottom of the battery. Ports 22 and 20 provide for the ingress and egress respectively of electrolyte, e.g., seawater, to the electrochemically active materials of the battery.

In Figures 2 and 3, the bipolar electrode assembly includes a barrier 24a made of a sheet of flexible plastics non-conductive material. For seawater electrolyte batteries, any waterproof dielectric sheet material may be used for the barriers such as polyethylene, polypropylene, or polystyrene. However, polyethylene terephthalate has been found to have better handling properties compared to other materials tested. In order to save space in the battery, or in other words to make the battery as small as possible, the barriers should be thin. However, they must be stiff enough to be self supporting and this puts a limit on the thinness of the barrier. It has been found that polyethylene terephthalate has the property of being stiff and otherwise more suitable than other available plastics sheet materials in the thickness range of .05 to .25 mm.

An anode 30 is located next to one face of the barrier 24a and a cathode 32 is located next to the opposite face of the barrier.

Normally the anodes or negative electrodes of seawater type batteries are metallic and are chosen from magnesium, zinc and aluminum, the active material of the cathodes or positive electrodes are sheets of chemically active material including the halides of metals such as lead chloride, silver chloride, or copper chloride, with a conductive metal screen or other conductive grid embedded therein. A fastening device 43, in this case a staple, penetrates the anode, the barrier and the cathode. It serves both to provide an intercell electrical connection from anode to cathode and to fasten both electrodes to the barrier, thus forming the bipolar assembly.

Other forms of intercell connections passing through anode, barrier and cathode include rivets and metallic clips. These also provide the double function noted above. Alternatively, a metallic or conductive plastics ribbon may be folded over an edge of the barrier to which the electrodes are contacted by pressing the battery together at the time of final assembly. These do not provide the support of the mechanical connector.

It should be noted that in other forms of bipolar electrodes where a metallic barrier is used, the electrical conductivity of the connector between anode and cathode will be many times greater than that of the fastening devices used in the present invention. However, since the devices to which the invention relates are used only at comparatively low rates of discharge, the fastening devices as discussed have proven to be satisfactory. Ports for transmission of electrolyte, such as those shown at 21 and 23, complete the bipolar subassembly.

It has been found that when batteries employing fasteners such as rivets or staples for intercell connectors passing through anode, barrier and cathode are discharged, particularly for long duration discharges, the cathode materials are electrochemically reduced and occupy less volume. This reduces the tightness of the contact and may cause a reduction in the battery performance. Therefore, it has been found advantageous

in batteries built for long duration discharges (say 8 hours or more) to have a portion of the cathode grid structure free of the cathode active material, and to make the electrical contact to the bare grid. This assembly is shown in Figure 4 in which a bare corner 33 of the cathode 32 is shown having a rivet 46a passing therethrough.

Figure 5 is a horizontal cross section of the battery of Figure 1 along the line 5—5. This battery comprises 4 cells. However, the invention has been used to advantage in batteries having up to 16 cells. The interior of the battery is divided into four cell compartments by the barriers 24a, 24b and 24c each barrier being located between each adjacent pair of cells of the battery, and each with its electrodes attached being a bipolar electrode subassembly. It is to be noted that endwall 16 supports an anode 30 on its inner face and that endwall 18 similarly supports a cathode 32 thus completing the first and fourth cell of the battery. Electrolyte spaces 34a, 34b, 34c and 34d are provided between the anode and cathode of each cell.

The electrolyte space 34 is preserved by plate spacing means. In the design of Figure 5, the means comprises a series of plastic buttons 36 adhered to the face of one of the electrodes, preferably the anode. Alternatively, sheeted materials such as non woven fabrics may be used for plate separation. In Figure 7, a connector 40, in this instance a rivet, electrically connected to the anode adjacent to endwall 16 passes through endwall 16 and is in turn connected to terminal wire 42, a similar arrangement provides a connection from the cathode attached to endwall 18 to terminal wire 44.

In seawater batteries of the type to which the present invention relates, there is a natural circulation of electrolyte from bottom to top of each cell. The circulation is due to a combination of temperature differentials, gas bubble formation and increase of density due to formation of partially soluble end products. The circulation of electrolyte is necessary to wash out the end products and provide fresh electrolyte for the duration of the discharge. This is well known in the art and numerous patents have issued relating to means of porting of cells and batteries. In order to obtain circulation in a battery of the type here discussed, it is necessary that the battery operate in a generally vertical position. This can be identified by being a position in which a first electrolyte port is above the second port. The orientation of the battery as shown in Figure 1 is the normal operating position as shown by the location of top port 20 and bottom port 22. The sidewalls 12a and 12b (Figure 5) and endwalls 16 and 18 (Figure 5) are in vertical planes and the top 14 and bottom 15 (Figure 7) are in horizontal planes.

The width of the barriers is somewhat greater than the width of the endwalls. At the time of battery assembly, two opposing edges of each barrier are folded over to form flanges. It is desirable that the flanges do not interfere with the ports such as 21, 23 (Figure 2) and therefore, in the construction shown, the flanges are formed on the vertical rather than the horizontal edges of the barriers. Sidewalls 12a and 12b formed of an adhesively coated tape are wrapped around endwalls 16 and 18 and contact the outer faces of each of the several flanges of the barriers. The faces of the flanges provide an adherence surface for the adhesive tape and serve to locate and hold the several bipolar assemblies with respect to the battery assembly as well as sealing off each cell compartment from the cells adjacent thereto. The construction is shown in Figure 6, an enlargement of the top corner of Figure 5. In Figure 6, 25a represents a flange formed on the vertical edge of barrier 24a, and 25b represents a flange formed on the vertical edge of barrier 24b.

Figure 7 depicts in section the battery of Figure 1 along the line 7—7. The anode 30 and cathode 32 are somewhat shorter than the full heights of the battery so as to leave top passages 50a, 50b, 50c and 50d and bottom passages 52a, 52b, 52c and 52d within the structure. The top passage 50a runs from sidewall 12a to sidewall 12b and is defined by the first endwall 16, the first barrier 24a and the top wall 14. Further, it is continuously open to the electrolyte space 34 of the first cell. The bottom passage 52a likewise runs from sidewall 12a to sidewall 12b and is defined by the bottom wall 15, the first endwall 16 and the first barrier 24a. The first bottom passage is continuously open to the electrolyte space 34 of the first cell. The top passages 50b, 50c, 50d and bottom passages 52b, 52c and 52d defined in turn by the barriers and the second endwall are associated with each of the succeeding cells of the battery. The several passages are connected together and to the outside by ports 20 and 21a, 21b and 21c.

Rivets 46a, 46b, and 46c, Figure 7, serve the same purpose of intercell connector and fastener as the staple 43 of Figure 3. Alternative constructions are shown in Figure 7 for the topwall and bottom wall of the battery. In the first construction, as shown at 14, a strip of adhesive tape is placed over the top or bottom of the battery and pressed down to contact the top or bottom edges of the barriers, the sidewalls and the endwalls of the battery. Alternatively, as shown at 15, the battery is dipped into a liquid plastic or hot melt material which is then permitted

to set so as to form a solidified material. One type of suitable plastic is epoxy resin. A typical hot melt may be a mixture of waxes, or natural rosins, as well known in the art. The second of these constructions is more rugged than the first.

In the manufacture of the cathodes described above, it is found that the support grid may be embedded into a sheet of the chosen cathode mix in such a manner that the grid is exposed on one surface of the cathode and distant from the opposite face. When such a cathode is used in a battery of the construction noted above, it has been found that the position of the grid with respect to the electrolyte and the barrier flanges is an important factor in achieving rapid activation. It has been found that the battery will activate more rapidly upon immersion if the face of the cathode having the grid exposed on its surface is in direct contact with the electrolyte and away from the barrier.

The flanges of the barriers may be folded either toward the anode side of the barrier or the cathode side. Where the cathode is thick and rugged, there is little choice as to the direction of the fold. However, when the cathode is thin and fragile, it is desirable to fold the flange forward the anode. By this practice, there is less chance of breaking the edges of the cathode which might result in poor performance and possible short circuitry of one or more cells.

In Figure 6, flange 25a is shown folded toward the cathode 32. Flange 25b is shown folded toward anode 30b.

Seawater batteries as built using the constructions noted above have been completely successful in test and in actual service discharges. Of particular interest, has been the ability of the battery to successfully withstand extreme environmental exposure including shock and vibration testing.

Figure 8 shows the voltage during discharge of a 16 cell lead chloride magnesium battery made in accordance with the present invention. From the 3 minute point to the end of the discharge the battery was immersed in a 3% saline solution at 30°C. and the load resistance was 87 ohms.

Figure 9 shows similar information resulting from the discharge of a 13 cell silver chloride magnesium battery under similar conditions.

WHAT WE CLAIM IS:—

1. A galvanic battery comprising a housing and a plurality of bipolar electrode assemblies in the housing, each assembly comprising an anode and a cathode which are electrically connected to each other and are separated from each other by a barrier made of a sheet of flexible non-conductive material having two opposed side edges each of which is bent to form a flange, the assemblies being arranged parallel to each other, face to face with spaces between them, and with the flanges of each assembly other than an end assembly directed towards an adjacent assembly, the flanges together with adhesively coated tapes which are sealed to the flanges forming sidewalls of the housing.

2. A battery according to claim 1, in which the thickness of each barrier is within the range of 0.05 to 0.20 mm.

3. A battery according to claim 1 or claim 2, in which the material of each barrier is polyethylene terephthalate.

4. A battery according to any one of the preceding claims, in which each cathode comprises a sheet of chemically active material and a conductive metal grid embedded in one surface thereof, the grid being exposed at the said surface and the opposing surface of the cathode being located adjacent the barrier.

5. A battery according to claim 4, in which a portion of the conductive metal grid is free of the cathode active material and in which the anode is electrically connected to this bare portion of the grid.

6. A battery according to any one of the preceding claims, in which the material of the anode consists of either zinc, magnesium or aluminium, and the active material of the cathode consists of either lead chloride, silver chloride or copper chloride.

7. A battery according to any one of the preceding claims, in which the electrical connection between the cathode and the anode penetrates the cathode, the barrier and the anode and thereby fastens the cathode and the anode to the barrier.

8. A battery according to any one of the preceding claims, in which each of the opposing flanges is bent in the direction of the anode attached to the face of the respective barrier.

9. A battery according to any one of the preceding claims, in which the housing includes end walls in addition to the sidewalls, and in which the tape of one sidewall is sealed to a first edge of the one end wall and to a first edge of the other end wall, the tape of the other sidewall being sealed to a second opposing edge of the first end wall and to a second opposing edge of the second end wall.

10. A battery according to claim 9, in which the housing further comprises a top-wall formed of an adhesively coated tape which is sealed to the tops of the end walls, to the tops of the sidewalls and to the tops of the barriers.

11. A battery according to claim 9 or claim 10, in which the housing further includes a bottom wall formed of an ad-

hesively coated tape which is sealed to the bottoms of the end walls, to the bottoms of the sidewalls, and to the bottoms of the barriers.

12. A battery according to claim 9, in which the housing includes a solid top wall attached to the tops of the end walls, to the tops of the sidewalls and to the tops of the barriers, the top wall bridging the spaces between end walls, barriers and sidewalls.

13. A battery according to claim 9, in which the housing includes a solid bottom wall attached to the bottoms of the end walls, the bottoms of the sidewalls and the bottoms of the barriers, the solid bottom wall bridging the spaces between end walls, barriers and sidewalls.

14. A battery according to any one of claims 9 to 13, further comprising an anode attached to the inner face of one end wall and a cathode attached to the inner face of the other end wall.

15. A battery according to claim 1, substantially as herein described with reference to the accompanying drawings.

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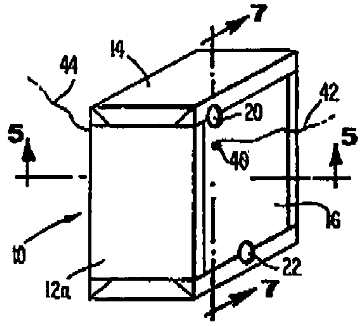

Fig. 1

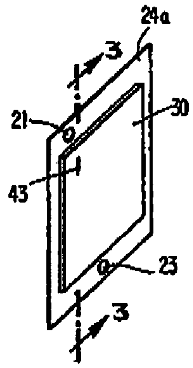

Fig. 2

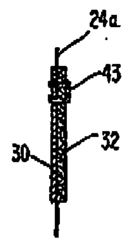

Fig. 3

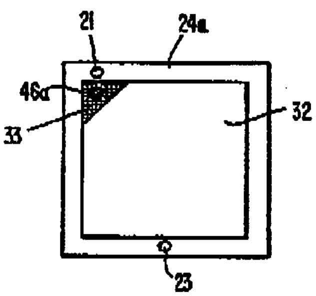

Fig. 4

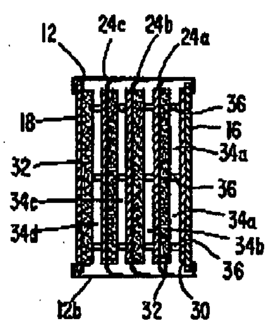

Fig. 5

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Sheet 2

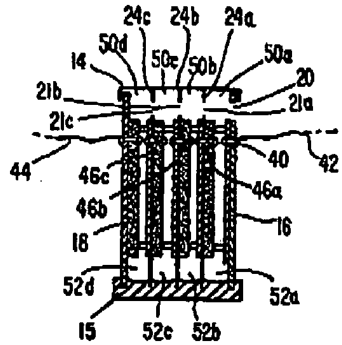

Fig. 7

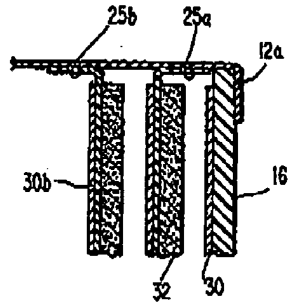

Fig. 6

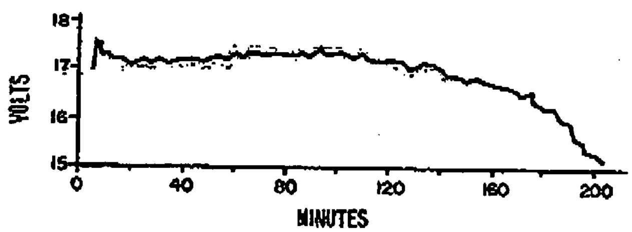

Fig. 8

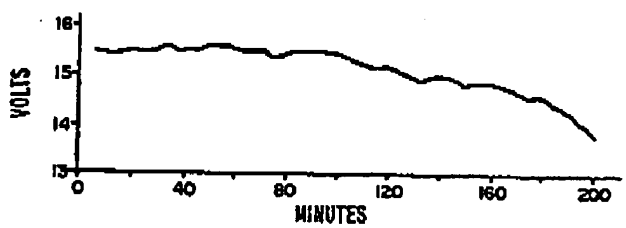

Fig. 9